

Formation of the SnO<sub>2</sub> Network with Hollow Structure from Water-Ethanol Mixed SolventMoon-Jin Hwang and Kwang-Sun Ryu<sup>†,\*</sup>

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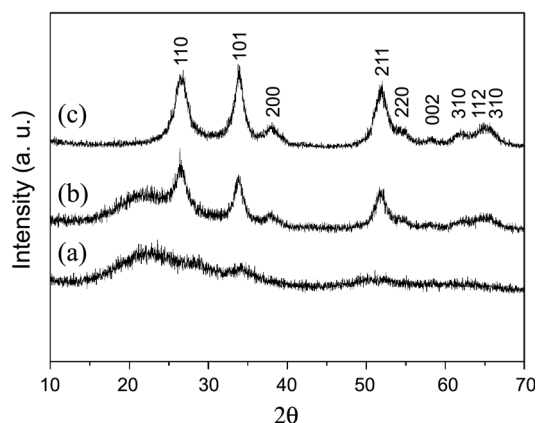
**Key Words** : SnO<sub>2</sub>, SnO<sub>2</sub> hollow, Nanostructure, Ethanol, Solvent

The SnO<sub>2</sub> network with hollow structures were obtained from SiO<sub>2</sub>/SnO<sub>2</sub> core-shell powder in water-ethanol mixed solvents at mild experimental conditions. SnCl<sub>2</sub> as SnO<sub>2</sub> source reacts partially with H<sub>2</sub>O and forms an insoluble salts in water (SnCl<sub>2</sub> + H<sub>2</sub>O → Sn(OH)Cl(s)).<sup>1</sup> This salts formation may be not desirable to protect an aggregation of Sn based materials, but we expect that the controllable addition of water into absolute alcohol containing Sn<sup>2+</sup> ions and hydrophilic SiO<sub>2</sub> spheres could help to promote the formation of homogeneous core-shell composites. It is suggested that a simple removal of SiO<sub>2</sub> template and a facile separation of porous structure can be obtained from the formation of SnO<sub>2</sub> network with hollow structure.

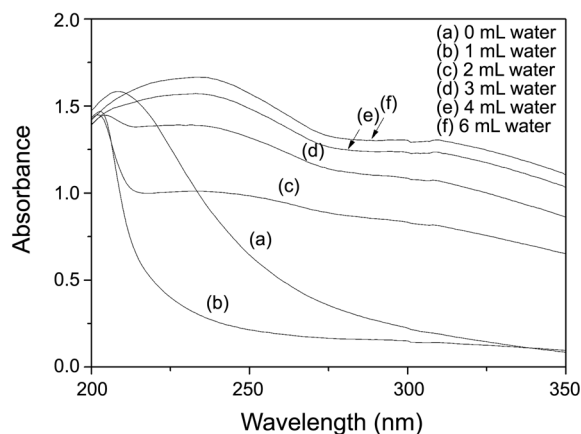
SiO<sub>2</sub> spheres were prepared according to well-known Stöber method.<sup>2</sup> SiO<sub>2</sub> with about 300 nm was obtained from the mixing of 0.2 M TEOS (tetraethylorthosilicate), 17 M H<sub>2</sub>O, and 0.6 M NH<sub>4</sub>OH in ethanol. SiO<sub>2</sub> was washed several times with ethanol and distilled water and heated at 350 °C. The 0.5 g of SiO<sub>2</sub> powder was added to 50 mL ethanol with ultrasonic wave irradiation. The 0.5 g of SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in the water-ethanol solution containing x mL water and 50-x mL ethanol (x = 0, 1, 2, 3, 4, and 6). The solution containing Sn<sup>2+</sup> ions was added slowly into the solution containing SiO<sub>2</sub> particles with stirring. The mixed solution was heated at 80 °C until the solvent was reduced to about 10 mL. The reduced solution was kept at room temperature until all solvent was evaporated. The resultant SiO<sub>2</sub>/SnO<sub>2</sub> precursors were dried at 100 °C. SiO<sub>2</sub>/SnO<sub>2</sub> particles were prepared by heating of SiO<sub>2</sub>/SnO<sub>2</sub> precursors at 350 °C for 5 hrs. SnO<sub>2</sub> hollow structures were obtained by the removal of SiO<sub>2</sub> from SiO<sub>2</sub>/SnO<sub>2</sub> particles with 1 N NaOH aqueous solution for 2 days. SnO<sub>2</sub> hollow structures were washed eight times with distilled water without centrifugation.

Figure 1 shows the representative XRD patterns of the samples. As shown in Figure 1(a), the peaks of SiO<sub>2</sub>/SnO<sub>2</sub> precursor obtained from pure ethanol contain both of the peaks of an amorphous SnO<sub>2</sub> precursor and the broad peak of an amorphous SiO<sub>2</sub>, centered at 2θ = 21.34° in the range of 15-25°. When SiO<sub>2</sub>/SnO<sub>2</sub> precursor was heated at 350 °C, a tetragonal SnO<sub>2</sub> phase was observed, as shown in Figure 1(b). In Figure 1(c), the peaks of SnO<sub>2</sub> hollow structure prepared from water-ethanol mixed solvent with 1 ml water were identified as SnO<sub>2</sub> (JCPDS file No. 01-070-6153) with a tetragonal lattice.

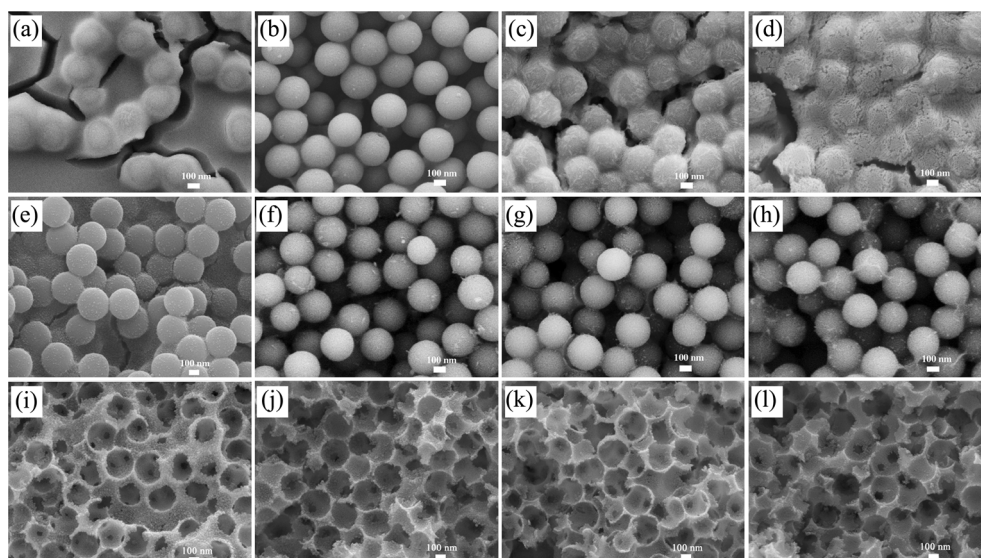
Figure 2 shows the UV-vis spectra of SiO<sub>2</sub> dispersed in water-ethanol mixed solvent with x mL water and (100-x) mL ethanol at room temperature. The UV absorption band of SiO<sub>2</sub> dispersed in pure ethanol solvent was centered at around 208 nm, whereas the center of absorption band of SiO<sub>2</sub> in water-ethanol mixed solvent with 1 mL water was shifted to lower wavelength, which is centered at around 205 nm, and its band width became narrower, as shown in Figure 2(a and b). In case of SiO<sub>2</sub> in water-ethanol mixed solvent with 2 mL water, the UV absorption shoulder located below 213 nm was centered at around 203 nm and the increase of



**Figure 1.** The representative XRD patterns of (a) SiO<sub>2</sub>/SnO<sub>2</sub> precursor, (b) SiO<sub>2</sub>/SnO<sub>2</sub> particle, and (c) SnO<sub>2</sub> hollow structure (a: pure ethanol, c: 1 mL water).



**Figure 2.** UV-vis spectra of the ethanol solutions containing SiO<sub>2</sub> and various amount of water (a: 0 mL, b: 1 mL, c: 2 mL, d: 3 mL, e: 4 mL, and f: 6 mL water).



**Figure 3.** The representative SEM images of (a-d)  $\text{SiO}_2/\text{SnO}_2$  precursors coated on a slide glass, (e-h)  $\text{SiO}_2/\text{SnO}_2$  particles, and (i-l)  $\text{SnO}_2$  hollow structures from different amount of water (0-6 mL).

absorbance between 213 nm and 350 nm was observed in Figure 2(c). In general, the change of UV-vis absorption band depends on the degree of solvent polarity and of solvent shell formation on solute.<sup>3</sup> It can be understood that the increase of solvent polarity by adding water into ethanol induces blue shift of UV absorption band with increasing electronic transition energy between ground state and excited state of  $\text{SiO}_2$  (Figure 2(a-d)). It is estimated that the broad absorption bands above 213 nm are caused by the increase of turbidity and the effect of solvent shell containing large water molecules on  $\text{SiO}_2$  resulting in the decrease of electronic transition energy (Figure 2(c-f)).

Figure 3 show the SEM images of the samples. Figure 3(a-d) shows the different shapes of  $\text{SiO}_2/\text{SnO}_2$  precursors coated on a slide glass.  $\text{SiO}_2/\text{SnO}_2$  precursors were prepared from water-ethanol mixed solvent with 0, 2, 4, and 6 mL water. The shape of discrete  $\text{SiO}_2$  particles coated with  $\text{SnO}_2$  precursors were obtained from pure ethanol. It indicates that the interaction force between  $\text{SiO}_2$  and  $\text{SnO}_2$  precursor is relatively weak. The homogeneous  $\text{SiO}_2/\text{SnO}_2$  precursors were obtained from the mixed solvent with 2 mL water. The increase of shell thickness with increasing the amount of water from 4 mL to 6 mL was caused by the increase of hydrated  $\text{Sn}^{2+}$  on  $\text{SiO}_2$ . Figure 3(e-h) shows the shapes of  $\text{SiO}_2/\text{SnO}_2$  particles prepared after heating of  $\text{SiO}_2/\text{SnO}_2$  precursors at 350 °C. After heating, the reduced shell thickness is because  $\text{H}_2\text{O}$  was removed from the hydrated form coated on  $\text{SiO}_2$ , as shown in Figure 3(g and h). Figure 3(i-l) shows the shapes of  $\text{SnO}_2$  hollow structures after the removal of  $\text{SiO}_2$  from  $\text{SiO}_2/\text{SnO}_2$  particles. The network structures with irregular pore shapes were observed in Figure 3(i, k, and l). The  $\text{SnO}_2$  network with homogeneous pore sizes was obtained from water-ethanol mixed solvent with 2 mL water, as shown in Figure 3(j).

Table 1 lists the EDS element analysis results for  $\text{SiO}_2/$

**Table 1.** EDS data of  $\text{SiO}_2/\text{SnO}_2$  particles and  $\text{SnO}_2$  hollow structures

| Sample                            | Composition of water-ethanol solvent |         | Weight % of element |       |       |      |      |
|-----------------------------------|--------------------------------------|---------|---------------------|-------|-------|------|------|
|                                   | Water                                | Ethanol | Si                  | O     | Sn    | Cl   | Na   |
| $\text{SiO}_2/$<br>$\text{SnO}_2$ | 0                                    | 100     | 35.81               | 36.64 | 27.05 | 0.50 | -    |
|                                   | 2                                    | 98      | 37.19               | 38.77 | 23.53 | 0.51 | -    |
|                                   | 4                                    | 96      | 34.04               | 33.09 | 32.14 | 0.73 | -    |
|                                   | 6                                    | 94      | 43.07               | 32.26 | 24.11 | 0.56 | -    |
| $\text{SnO}_2$<br>hollow          | 0                                    | 100     | 0.94                | 17.12 | 80.70 | 0.44 | 0.80 |
|                                   | 2                                    | 98      | 0.87                | 17.43 | 80.74 | 0.23 | 0.73 |
|                                   | 4                                    | 96      | 0.82                | 16.26 | 81.68 | 0.33 | 0.91 |
|                                   | 6                                    | 94      | 0.71                | 21.51 | 76.41 | 0.25 | 1.12 |

$\text{SnO}_2$  particles and  $\text{SnO}_2$  hollow structures. The EDS results show that the Cl element contents were reduced to 0.50-0.73 wt % during heating process of  $\text{SiO}_2/\text{SnO}_2$  precursors. After NaOH treatment and several washing process, the Si contents of  $\text{SnO}_2$  hollow structures were 0.71-0.94 wt %.

It is expected that the facile formation of  $\text{SnO}_2$  network with hollow structure can increase the yield efficiency in mild separation process and reduce the efforts and the energies to obtain  $\text{SnO}_2$  hollow structure.

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## References

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